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PATENT SPECIFICATION

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DRAWINGS ATTACHED

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(54) PRODUCTION OF HYDROXYLAMMONIUM SALT

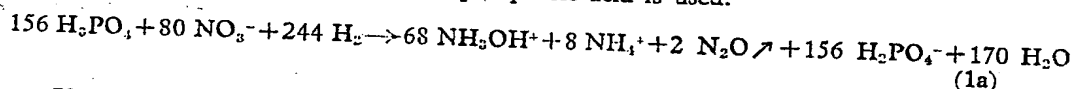
(71) We, STAMICARBON N.V., a Netherlands Limited Liability Company, of 2 van der Maesenstraat, Heerlen, the Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an improved continuous process for the preparation of a solution of E3 hydroxylammonium dihydrogen phosphate or hydroxylammonium ammonium sulphate in water to provide a higher concentration of hydroxylammonium salt in the final solution and particularly relates to such processes employing nitrate ions in which free nitric acid is substantially absent from the starting solution.

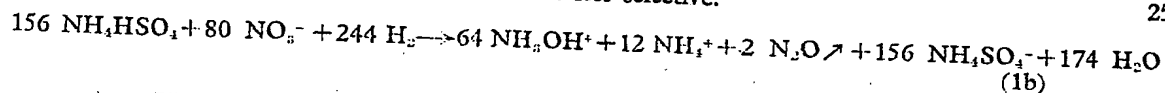
A known continuous process for the preparation of a hydroxylammonium salt solution comprises the catalytic reduction of nitrate ions at the surface of a noble metal by means of molecular hydrogen in a weakly acid buffered solution, starting from make-up solutions which contain nitrate ions and also the relatively weak acids phosphoric acid or ammonium hydrogen sulphate. The nitrate ions may be introduced into the feed stream by adding free nitric acid thereto, or by absorbing nitrogen oxide vapours therein.

Reduction of nitrate ions to ammonium ions, nitrogen and nitrous oxide takes place as secondary reactions during the process. In a continuous process using a palladium catalyst at 25°C it has been found that the chemical reactions taking place may be represented by the following overall equations, which do not take into account the formation of nitrogen.

In equation (1a) a solution of phosphoric acid is used.



If the process is carried out in an ammonium hydrogen sulphate solution as shown in equation (1b), the reduction is somewhat less selective.



The nitrate ions to be reduced are introduced to the hydroxylamine synthesis reactor in the form of a solution containing a relatively weak acid, namely phosphoric acid or ammonium hydrogen sulphate. A relatively weak acid is used because if a make-up solution containing free nitric acid is added to the reaction medium, failure of the supply of hydrogen would result in the catalyst being deactivated, or being dissolved if a palladium catalyst is used. This risk of the catalyst being damaged increases as the concentration of free nitric acid in the reaction medium becomes higher. To avoid such difficulties it has been proposed to carry out the hydroxylamine formation in a buffered solution in which the quantity of nitric acid is reduced to a negligible value by the buffer action.

If however it is desired to use nitric acid as a source of make-up nitrogen for the hydroxylamine production, said nitric acid may first be converted using a buffer salt in a process stream leading to the synthesis zone, into a nitrate and the acid from which the buffer salt is derived, which acid is substantially weaker than nitric acid.

Buffer salts which may be used for the purpose are alkali metal or ammonium hydrogen phosphates, or alkali metal or ammonium sulphates, which react with nitric

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acid to form the alkali metal or ammonium nitrates and phosphoric acid, or alkali metal hydrogen sulphate or ammonium hydrogen sulphate. In a continuous process where a hydroxylamine synthesis zone and an oxime synthesis zone utilizing the hydroxylamine are connected through a circulating buffered aqueous solution of buffer salt and buffer acid, make-up nitric acid is supplied to the solution flowing from the

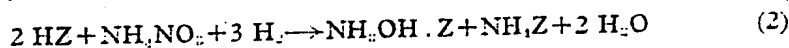
5 salt and buffer acid, make-up nitric acid is supplied to the solution flowing from the oxime synthesis zone to the hydroxylamine synthesis zone. In the hydroxylamine synthesis zone the solution takes up hydroxylamine which combines with the buffer acid present in the solution to form the hydroxylammonium salt, and in the oxime synthesis zone the hydroxylammonium ion is utilized in the formation of oxime, during which

10 reaction one mole of the acid corresponding to the hydroxylammonium salt is liberated for each mole of this salt, the acid being fed back to the hydroxylamine synthesis zone by the continuously circulating solution.

The process may be represented by the following reaction equations, in which NH_4^+ may be replaced by alkali metals, and where Z stands for the H_2PO_4^- or the NH_4SO_4^- radical. Equations 2 and 3 are part equations. For the sake of simplicity of the following equations the formation of byproducts such as NH_4^+ and N_2O has been omitted, just as the fact that in solution NH_4SO_4^- will be in equilibrium with NH_4^+ and SO_4^{2-} .

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I. Hydroxylamine synthesis with formation of the hydroxylammonium salt:

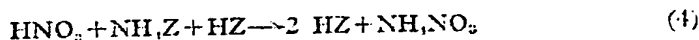


II. Oxime formation by reaction with cyclohexanone of the resulting solution containing hydroxylammonium salt:



III. Supply of make-up HNO_3 , after removal of the oxime formed, with formation of a fresh starting solution suitable for the hydroxylamine synthesis:

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Thus in theory after the addition of make-up HNO_3 a solution is obtained which has the same molar

$$\frac{\text{NH}_4\text{NO}_2}{\text{HZ}}$$

ratio as the solution used as the reaction medium for the hydroxylamine synthesis according to equation (2). In practice said solution contains, besides the acid HZ, a certain quantity of the buffer salt NH_4Z , because some ammonia is formed with the hydroxylamine (see equations 1a and 1b).

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In practice the pH of the hydroxylamine synthesis zone is maintained at a value of from 0 to 3, and preferably at a value of approximately 1.8 to 2.0; the pH in the oxime synthesis zone then varying from the pH in the hydroxylamine synthesis zone to zero, preferably not lower than 0.3. According to equation (4), the solution to which make-up nitric acid is added will have to contain at least one mole of the salt NH_4Z per mole of nitric acid, in order that free nitric acid be virtually absent in the make-up liquid. In such a solution virtually free of nitric acid all dissolved H^+ ions are considered to originate from the relatively weak acid HZ, so that said H^+ ion concentration can never exceed the Z^- ion concentration.

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According to equation (2) the use of such a make-up solution results in a hydroxylamine-containing solution which contains one mole of NH_4Z per mole of hydroxylammonium salt.

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An increase of the hydroxylamine content of the solution automatically causes an increase of the NH_4Z content, which given the moderate solubility of NH_4Z compared to NH_4NO_2 , sets a limit to the hydroxylammonium salt content.

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It is however important in practice to work with as highly concentrated solutions as possible, since this will allow a reduction of the cost of capital investment and operating costs, e.g. as the pumping cost for circulating the liquid. It would be possible

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to work with more highly concentrated solutions by carrying out the synthesis at a higher temperature, for instance 60°C instead of 20°C, so that solutions might be used which crystallize out at the lower temperature but are still unsaturated at 60°C. An objection against such a procedure is that such solutions might cool to temperatures below the crystallization point in case of a breakdown in the process, so that various conduits might get clogged and it would be difficult to restart the process.

Another disadvantage is that solutions with a high content of hydroxylammonium salt and a corresponding quantity of the ammonium salt have a high viscosity which not only substantially increases the cost of circulating the process fluid, but also results in difficulties due to poorer dissipation of the reaction heat and more difficult separation of the catalyst from the hydroxylamine-containing solution produced.

It is the object of the present invention to provide feed solutions for the hydroxylamine synthesis which have a high hydroxylamine content coupled with a low crystallization temperature and a low viscosity, i.e. contain less ammonium salt (apart from ammonium nitrate), while still meeting the requirement of being virtually free of nitric acid, so that the molar

$$\frac{[H^+]}{[Z^-]}$$

ratio in said solutions is ≤ 1 , where Z is the H_2PO_4 or NH_4SO_4 radical or a mixture of such radicals, and $[H^+]$ is the concentration of the weak acid HZ.

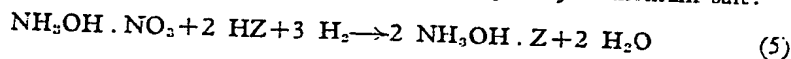
The invention provides in a process for the preparation of hydroxylammonium dihydrogen phosphate or hydroxylammonium ammonium sulphate by the catalytic reduction in a reactor of nitrate ions with molecular hydrogen in which nitric acid is normally present in the feed stream to the reactor the step of introducing hydroxylammonium dihydrogen phosphate or hydroxyl ammonium ammonium sulphate into the said feed stream in a proportion such that the feed stream contains substantially no free nitric acid in entering the said reactor.

Thus to obtain a starting solution in which free nitric acid may be considered absent according to the invention, it is not necessary for the feed solution to contain at least one mole of ammonium dihydrogen phosphate or one mole of ammonium sulphate per mole of nitric acid added. In one embodiment hydroxylammonium salt formed in the hydroxylamine zone is used for removing free nitric acid from the nitrate-ion containing stream entering the hydroxylammonium salt synthesis zone.

In a practical embodiment of the invention a solution containing hydroxylammonium salt is bled off from a continuous product stream leaving the hydroxylammonium salt synthesis zone, and this bleed stream is mixed with the stream of solution returning from the oxime synthesis zone which contains little or no hydroxylammonium salt and into which recycle stream fresh make-up nitric acid is introduced, the proportion of hydroxylammonium salt introduced into the said recycle stream being such that the final stream introduced into the hydroxylammonium salt synthesis zone contains at least one mole of hydroxylammonium salt per mole of nitric acid.

This process may be represented by the following reaction equations, where Z again stands for the H_2PO_4 or the NH_4SO_4 radical or for a mixture of the two. Equation 5 is a part equation

I. Hydroxylamine synthesis with formation of the hydroxylammonium salt:

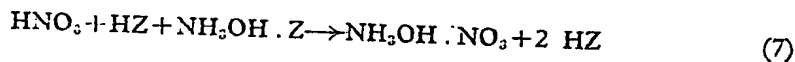


1 mole of $NH_2OH \cdot Z$ is recirculated (see equation 7).

II. Oxime formation by reaction with cyclohexanone of the hydroxylammonium salt resulting solution containing:



III. Supply of make-up HNO_3 and recycled hydroxylammonium salt, after removal of the oxime formed, to obtain a make-up liquid suitable for the continuous hydroxylamine synthesis:



These equations show that the concentration of nitrate ions may be higher in the make-up liquid obtained according to equation (7) than in the make-up liquid obtained according to equation (4).

For the concentration of nitrate ions that can be reached in the make-up liquid obtained according to equation (4), and therefore also the hydroxylamine concentration that can be reached by reduction of said nitrate ions, depends on the concentration of the moderately soluble salt NH_4Z in the solution to which nitric acid is added, whereas in the make-up liquid obtained according to equation (7) the concentration of nitrate ions that can be reached depends on the concentration of $\text{NH}_4\text{OH} \cdot \text{Z}$ (which has a higher solubility than NH_4Z) in the solution to which nitric acid is added.

A particular embodiment of the invention is hereinafter described and illustrated in the accompanying drawing, which is a schematic representation of apparatus for the hydroxylamine synthesis with associated apparatus for the oxime synthesis.

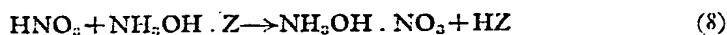
Referring to the drawing, the apparatus comprises a hydroxylamine synthesis reactor (A), provided with an agitator (13), a filter (14) or other suitable solid/liquid separator, and a distributing device (15) for distributing the hydrogen to be supplied through a conduit (9). The nitrate-containing make-up liquid is supplied through a conduit (1), the hydroxylamine-containing solution is continuously discharged through a conduit (2), and the waste gases are discharged through a conduit (10).

The reactor is filled with a suspension of a catalyst e.g. a palladium catalyst. Filter (14) prevents catalyst particles being discharged with the hydroxylamine-containing liquid.

The hydroxylamine-containing solution is fed through conduits (2, 4) to the oxime synthesis zone (B), where the oxime formation takes place in a process in which there is a counter-current flow of cyclohexanone supplied through a conduit (11). The oxime formed is discharged through a conduit (12) and the solution impoverished or exhausted in hydroxylamine returns to the hydroxylamine synthesis reactor through a conduit (5), a crystallization and/or evaporation unit (C), and conduits (7, 1).

Reaction water and still undissolved cyclohexanone, and if necessary ammonium salt continuously formed in a secondary reaction taking place as well as the hydroxylamine reaction, are removed from apparatus (C) through a conduit (6). Make-up nitric acid is supplied through a conduit (8). The supply of make-up nitric acid can also be effected by absorption of nitrous vapours in the liquid exhausted in hydroxylamine, when nitric acid is formed in situ.

The operation according to the invention is effected by the use of a conduit (3) which bleeds off product solution containing hydroxylammonium salt discharged through conduit (2) in a proportion so that all free nitric acid present in the liquid flowing through conduit (7) is neutralized, according to the reaction represented by the partial equation:



where Z stands for the H_2PO_4 or the NH_4SO_4 radical.

The following Examples and comparative experiment are provided using the apparatus hereinbefore described and illustrated in the accompanying drawing.

Comparative Experiment

A solution exhausted in hydroxylamine leaving the oxime synthesis zone through conduit (5), contained in addition to 2.3% by weight of cyclohexanone:

112 moles of H_2PO_4 ,
88 moles of $\text{NH}_4\text{H}_2\text{PO}_4$,
68 moles of NH_4NO_3 and
2238 moles of H_2O .

After removal of dissolved cyclohexanone, water and some ammonium nitrate in (C), and after addition of 88 moles of nitric acid through conduit (8), there resulted a make-up liquid for the hydroxylamine synthesis which was free of nitric acid and which contained:

200 moles of H_2PO_4 ,
148 moles of NH_4NO_3 and
2000 moles of H_2O .

The hydroxylamine-containing solution produced from the said liquid at 60°C and

a H_2 pressure of 9 atmospheres absolute, which was to be discharged through conduits (2, 4), contained:

44 moles of H_3PO_4 ,
68 moles of $NH_4OH \cdot H_2PO_4$,
88 moles of $NH_4H_2PO_4$,
68 moles of NH_4NO_3 and
2170 moles of H_2O

The said solution had a crystallization temperature lower than $15^\circ C$ and a viscosity measured at $60^\circ C$ of 1.6 kg/m.sec.

Said solution contained 13%, by weight (1.0 mole/kg) of hydroxylammonium dihydrogen phosphate.

Example 1

A solution exhausted in hydroxylamine, leaving the oxime synthesis zone through conduit (5), contained in addition to 2.5% by weight of cyclohexanone:

92 moles of H_3PO_4 ,
8 moles of $NH_4H_2PO_4$,
36 moles of NH_4NO_3 and
1238 moles of H_2O .

After removal of dissolved cyclohexanone, reaction water and some ammonium salt, and after addition of nitric acid, the process liquid in conduit (7) had the following composition:

100 moles of H_3PO_4 ,
80 moles of HNO_3 ,
36 moles of NH_4NO_3 and
1000 moles of H_2O .

After this solution has been mixed with the hydroxylamine-containing solution produced in reactor (A) and supplied through conduits (2, 3) in a ratio of 1.0 kg to 1.06 kg, the process fluid free of nitric acid flowing through conduit (1) consisted of:

205.3 moles of H_3PO_4 ,
71.6 moles of $NH_4OH \cdot NO_3$,
82.3 moles of NH_4NO_3 and
2232 moles of H_2O .

The hydroxylamine solution produced from this process fluid, which flows from reactor (A) to the oxime synthesis zone (B) through conduits (2, 4), had the following composition:

24 moles of H_3PO_4 ,
68 moles of $NH_4OH \cdot H_2PO_4$,
8 moles of $NH_4H_2PO_4$,
36 moles of NH_4NO_3 and
1170 moles of H_2O .

The crystallization temperature of this solution was lower than $15^\circ C$ and its viscosity was 1.6 kg/m.sec measured at $60^\circ C$, and 3.8 kgm/sec measured at $20^\circ C$.

The solution contained 24.7% by weight (1.88 moles/kg) of hydroxylammonium dihydrogen phosphate.

Compared to the comparative Experiment, this corresponded to an increase in concentration by 88%.

Example 2

Addition of nitric acid to the process fluid leaving evaporator (C) resulted in a solution flowing through conduit (7) which has the following composition:

100 moles of H_3PO_4 ,
80 moles of HNO_3 ,
26 moles of NH_4NO_3 and
500 moles of H_2O .

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Example 5
After addition of make-up nitric acid, the process fluid flowing through conduit (7) contained:

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1. In a process for the preparation of hydroxylammonium dihydrogen phosphate or by hydroxylammonium ammonium sulphate by the catalytic reduction in a reactor of nitrate ions with molecular hydrogen in which nitric acid is normally present in the

feed stream to the reactor, the step of introducing hydroxylammonium dihydrogen phosphate or hydroxylammonium ammonium sulphate into the said feed stream in a proportion such that the feed stream contains substantially no free nitric acid on entering the said reactor.

5 2. A process according to Claim 1, wherein product hydroxylammonium salt passes from the said reactor to an oxime-forming zone, and a recycle stream free of oxime is recycled to the said reactor, and make-up nitrate ions are present in the said recycle stream in the form of free nitric acid therein, and a proportion of the hydroxyl-
10 ammonium salt product stream is bled from the said product stream into the said recycle stream.

3. A process according to Claim 2, in which the nitrate ions in the recycle stream are obtained by introducing free nitric acid into the said recycle stream.

4. A process according to Claim 2, in which the nitrate ions in the recycle stream are obtained by absorbing nitrogen oxide vapour into the said recycle stream.

15 5. A process according to any of Claims 1 to 4 wherein the reaction medium in the said reactor is buffered with phosphoric acid or ammonium hydrogen sulphate to a pH of from 0 to 3.

6. A process for the production of a hydroxylammonium salt as claimed in Claim 1, substantially as hereinbefore described.

20 7. A process for the production of a hydroxylammonium salt substantially as hereinbefore described in the accompanying drawing or in any of the Examples.

8. Hydroxylammonium salt prepared by a process according to any of Claims 1 to 6.

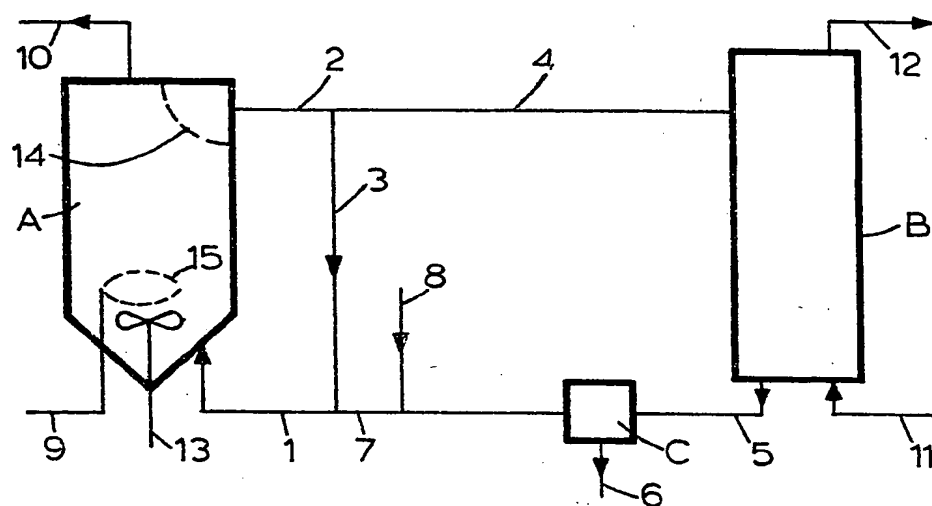
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1 SHEET

COMPLETE SPECIFICATION

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